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MEASUREMENT OF SALINITY OF SEA WATER

JERRY H. SERVICE

Special Publication No. 147

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U. S. COAST AND GEODETIC SURVEY
E. LESTER JONES, DIRECTOR

MEASUREMENT OF SALINITY OF SEA WATER

BY

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PREFACE

Excepting the preliminary calibration of the dipping refractometer to measure the salinity of sea water and of boiler water, this publication merely studies methods already available. Such slight modifications have been made in these methods as seemed to make them best suited to the hydrographic work of the Coast and Geodetic Survey.

Concerning the manipulation of the hydrometer at sea, valuable suggestions were received from reports on its use in the echo-sounding work of the Coast and Geodetic Survey ship *Surveyor*.

In connection with the titration method, valuable help was given by Roger C. Wells, of the United States Geological Survey, and by J. W. Sale, of the Food, Drugs, and Insecticides Administration. Through the courtesy of Mr. Sale, the samples used in the preliminary refractometer calibration were standardized, both by pycnometer and by chlorine titration, by the latter organization. For the excellent photograph of the refractometer the author is indebted to the manufacturers, the Bausch & Lomb Optical Co.

For information concerning the electrical conductivity method the author is indebted to Dr. Frank Wenner, of the Bureau of Standards, and to Dr. G. Guében, of the University of Liege.

The sinker method described by Mr. Cummings and used at the Scripps Institution of Oceanography was made known to the writer by Dr. George F. McEwen of that institution.

The tests made, and the present resultant publication, were made possible largely by the interest and encouragement of W. E. Parker, chief of the division of hydrography and topography of the Coast and Geodetic Survey, and K. T. Adams, commanding officer of the survey ship *Lydonia*. Thanks are also due the many other members of this bureau who cooperated in the work.

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MEASUREMENT OF SALINITY OF SEA WATER

By Jerry H. Service, *United States Coast and Geodetic Survey*

INTRODUCTION

This publication has to do with methods available for use on board ship for measuring the proportion of total dissolved solids in sea water. The adoption of echo sounding for hydrographic surveys made necessary a study of the speed of sound in sea water and its variation with the depth and with the temperature and the salinity of the water. The effect of salinity upon the speed of sound is not great; a change of salinity through the whole range encountered in ocean waters produces scarcely more than 1 per cent change in speed. The accuracy requirements of this bureau demand, however, that the hydrographer shall determine the salinity of the water in which soundings are being made to the nearest gram per kilogram (part per thousand); that is, to two significant figures.

It becomes necessary, then, to provide one or more standard methods that are simple of execution and that will give on board a moving ship and even in unskilled hands an accuracy such that there will be no doubt of the second significant figure of the result, and preferably a range of uncertainty in the third figure of not more than two or three units.

Two inexpensive methods have been found that are satisfactory. When the motion of the ship is not great, hydrometers of good quality that have been calibrated have been found to give satisfactory results when properly used; and for use in any ordinary weather suitable for hydrography a chemical titration method has been worked out that requires little or no previous experience for its successful manipulation.

The writer has calibrated the dipping refractometer to give salinity of sea water. Although the apparatus involved is rather expensive, so that probably it will not be supplied generally to the ships of the bureau, it is quite simple and easy to manipulate and will give good results on board ship even in the roughest weather.

It seems probable that an inexpensive electrical conductivity method can be worked out that will be easy of manipulation and give results adequate for the needs of the bureau. At the present time, however,

with the possible exception of the apparatus of Monsieur and Madame Chauchard, available conductivity apparatus is too expensive for the purposes of this bureau, principally because more precise than the requirements demand.

The method of obtaining salinity by the method of balancing columns of liquids is given brief mention in the pages that follow. Finally, two standard laboratory methods, the pycnometer method and the sinker method, respectively, are discussed briefly.

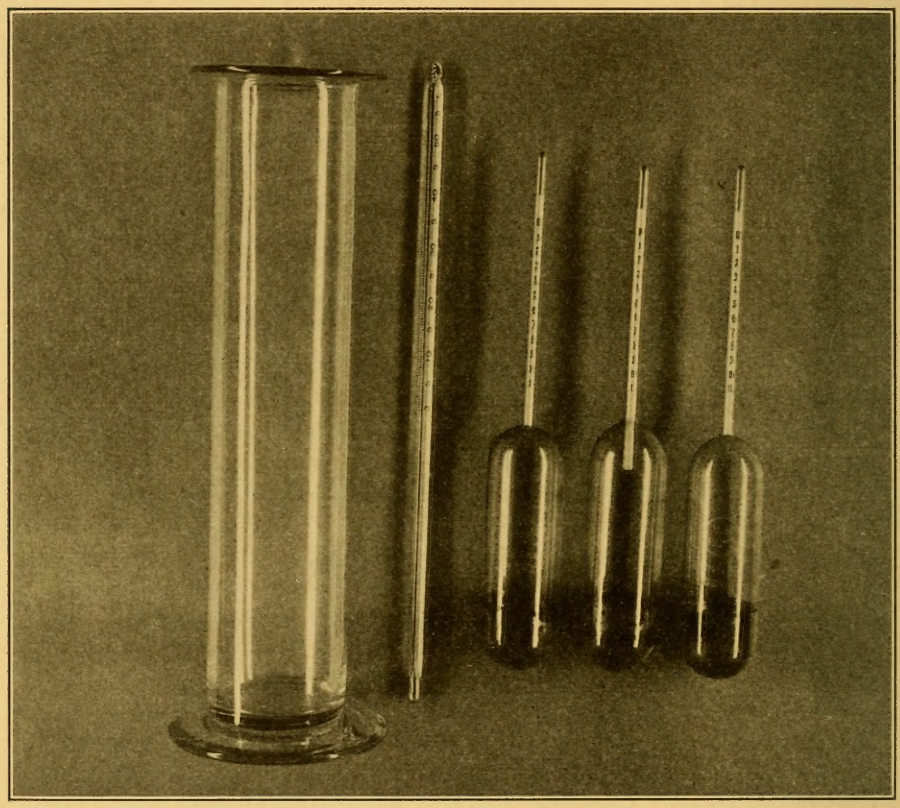


FIG. 1.—Hydrometer set

HYDROMETER METHOD

Hydrometer sets are furnished to ships of this bureau, as illustrated in Figure 1. The three hydrometers cover the specific-gravity range from that of fresh water to the greatest specific gravity likely to be encountered in ocean waters. Calibration data are furnished for the three hydrometers. The set includes also a 0° to 50° C. thermometer and a hydrometer jar. The following procedure is suggested for the use of the hydrometer:

Pour the sea water to be tested into the hydrometer jar to such depth that, when the hydrometer is put in, the water will not over-

flow. Stir the water with an unpainted stick. Observe the temperature to the nearest tenth of a degree. Put the hydrometer into the jar and steady it from spinning. Holding the top of the jar between the thumb and first or second finger, allow the jar to hang freely, so that the water surface is seen from below through the glass and the liquid. Slowly lower the jar until the ellipse becomes a straight line, which is the bottom of the water meniscus in the jar. The intersection of this straight line with the hydrometer scale will give the correct reading of the hydrometer. This reading should be made carefully to the nearest half division; that is, to one in the fourth decimal place of specific gravity.

TABLE 1.—*Apparent specific gravity of sea water*

[As indicated by a glass hydrometer with no errors of graduation]

Salinity in parts per 1,000	Temperature in degrees centigrade						
	0	5	10	15	20	25	30
28	1.02212	1.02191	1.02141	1.02062	1.01961	1.01837	1.01690
29	1.02292	1.02270	1.02218	1.02138	1.02036	1.01911	1.01764
30	1.02372	1.02348	1.02295	1.02214	1.02112	1.01986	1.01839
31	1.02453	1.02428	1.02374	1.02292	1.02188	1.02062	1.01914
32	1.02533	1.02506	1.02451	1.02368	1.02263	1.02136	1.01988
33	1.02614	1.02586	1.02529	1.02445	1.02340	1.02212	1.02063
34	1.02694	1.02664	1.02607	1.02522	1.02415	1.02287	1.02138
35	1.02774	1.02744	1.02685	1.02599	1.02492	1.02363	1.02213
36	1.02855	1.02824	1.02763	1.02676	1.02569	1.02439	1.02288
37	1.02935	1.02902	1.02841	1.02753	1.02644	1.02514	1.02363

Two or three readings should be taken, the hydrometer being disturbed between readings, to insure against a reading made with the bulb sticking to the side of the jar. It will be advisable to stir the water and make a second temperature observation after the hydrometer has been removed from the jar. The mean of the temperatures taken before and after the hydrometer readings should be used.

At the conclusion of the observations the hydrometer, thermometer, stirring rod, and hydrometer jar should be well rinsed with fresh water.

From the specific-gravity and temperature observations the salinity of the sample can be obtained conveniently by the use of the chart, Figure 2, or by Table 1, below If the temperature is measured correctly to the nearest tenth of a degree centigrade and the specific gravity to one in the fourth decimal place, the resulting value of salinity will be correct to within one or two units in the third significant figure.

In using Figure 2, which will be more convenient than Table 1, the point is found that corresponds to the observed temperature and specific gravity, both corrected for instrumental errors. The position of this point will show at once the first two significant figures of salinity. The third figure is obtained by estimating the frac-

tional part of the distance between the curves, measured parallel to the axis of specific gravities, that the point lies to the right of the curve of lower salinity. Thus, if the point lies three-tenths of the way from the 34 curve to the 35 curve, the salinity of the sample is 34.3, and so on.

If it should be desired to use Table 1 instead of Figure 2, it will be found convenient to reduce the observed specific gravity (corrected for graduation error) to the temperature in the table that is nearest to the observed temperature. For example, suppose that the observed specific gravity (corrected for graduation error) is 1.0224 and the temperature, 22.°3 C. It will be seen in the table that the change per degree in the specific gravity is 2.5 in the fourth decimal place (in the part of the table corresponding to the observed specific gravity and temperature). Hence the change for 2.3 degrees will be 6 in the fourth decimal place. Thus the observed specific gravity and temperature are equivalent to 1.0230 at 20° C. By interpolation between 1.02263 and 1.02340 we find the salinity of the given sample to be 32.5.

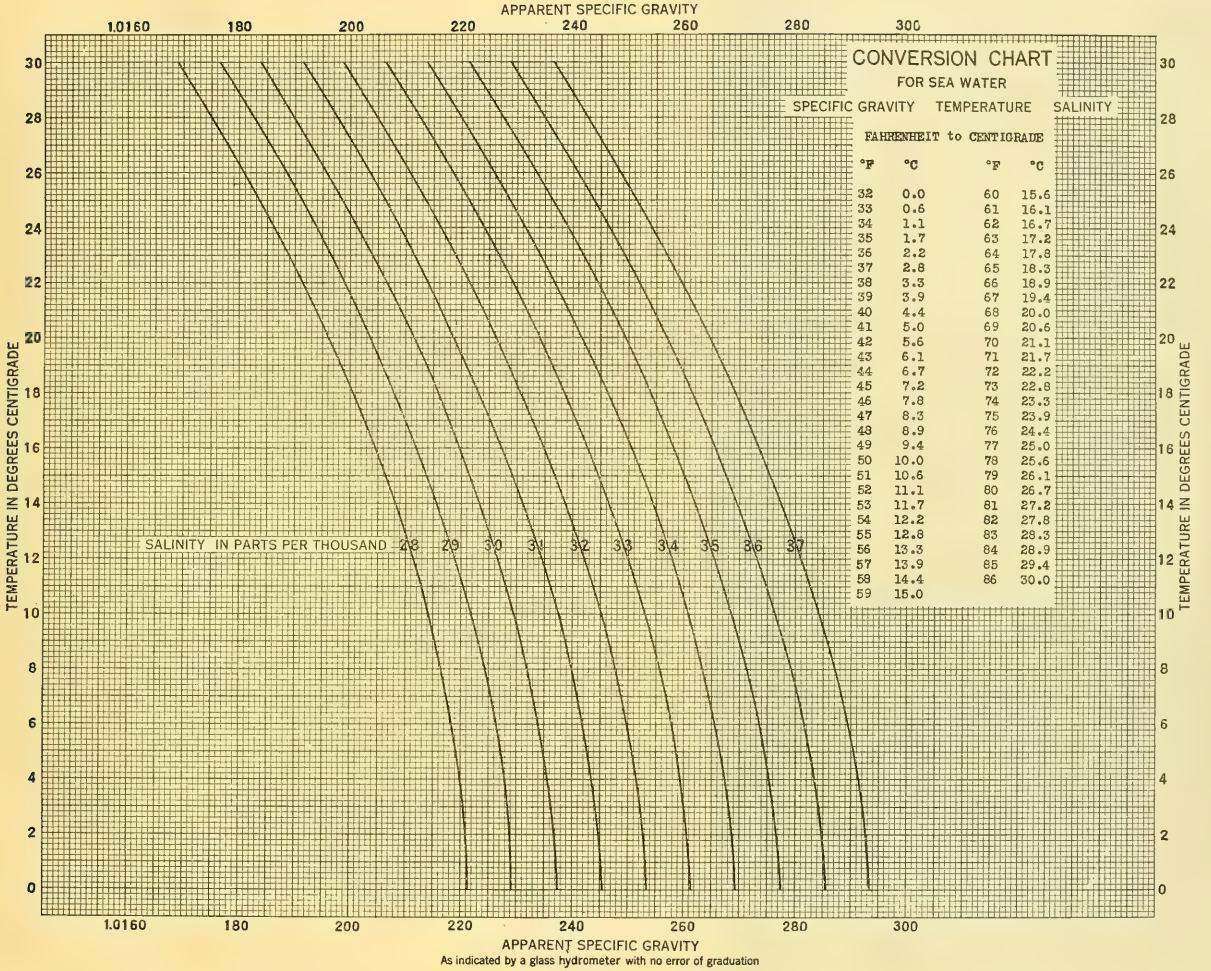
It will be seen from the table that a change of one unit in the second figure of salinity corresponds to a change of 7 or 8 in the fourth decimal place of specific gravity. Therefore, an error of one in the fourth decimal place of specific gravity will produce an error in the salinity scarcely greater than one in the third significant figure.

Experiments were conducted recently on board the *Lydonia* to determine how consistently a hydrometer could be read on board ship when the ship was under way and rolling and pitching gently to a light chop and swell. Several officers made independent specific-gravity and corresponding temperature measurements upon the same sample, with the results shown in Table 2. It will be seen from the table that the greatest discrepancy from the mean was one unit in the fourth decimal place of specific gravity.

TABLE 2.—*Independent determinations of the salinity of a given sample of sea water by the hydrometer method*

Observer No.	Observed specific gravity	Temperature, °C.	Specific gravity reduced to 20° C.
1	1. 02395	21. 8	1. 02441
2	1. 02395	21. 8	1. 02441
3	1. 02405	21. 7	1. 02449
4	1. 0240	21. 7	1. 0244
5	1. 0239	21. 9	1. 0244
6	1. 02385	21. 8	1. 02441
7	1. 0240	21. 7	1. 0244
8	1. 0239	21. 9	1. 0244
Mean			1. 02442

NOTE.—The above observations were made on board the Lydonia while she was under way and rolling and pitching to a light chop and swell.



CONVERSION CHART

FOR SEA WATER

SPECIFIC GRAVITY TEMPERATURE SALINITY

FAHRENHEIT to CENTIGRADE

°F	°C	°F	°C
32	0.0	60	15.6
33	0.6	61	16.1
34	1.1	62	16.7
35	1.7	63	17.2
36	2.2	64	17.8
37	2.8	65	18.3
38	3.3	66	18.9
39	3.9	67	19.4
40	4.4	68	20.0
41	5.0	69	20.6
42	5.6	70	21.1
43	6.1	71	21.7
44	6.7	72	22.2
45	7.2	73	22.8
46	7.8	74	23.3
47	8.3	75	23.9
48	8.9	76	24.4
49	9.4	77	25.0
50	10.0	78	25.6
51	10.6	79	26.1
52	11.1	80	26.7
53	11.7	81	27.2
54	12.2	82	27.8
55	12.8	83	28.3
56	13.3	84	28.9
57	13.9	85	29.4
58	14.4	86	30.0
59	15.0		

FIG. 2

103509—28. (Face p. 4.)

CHEMICAL TITRATION METHOD

This method consists in determining how much silver nitrate solution of known strength must be added to a measured sample of sea water to precipitate the chlorine in the sample as silver chloride. The proportion of chlorine in the total dissolved solids is nearly constant in ocean waters, so that the amount of nitrate solution required is a measure of the salinity of the sample. The observer is enabled to detect the completion of the precipitation by the addition of a small quantity of potassium chromate solution to the sea-water sample before any silver nitrate is added. As soon as the last trace of chlorine has been precipitated the next drop of nitrate solution added begins the precipitation of silver chromate, which is of a deep red color and brings about a sharp color change.

It is customary to let the silver nitrate solution run down into the measured sea-water sample from a burette. The level of solution in the burette is set at zero at the beginning, and the reading of the burette at the change of color will be the number of cubic centimeters of nitrate solution required to precipitate all the chlorine from the sample. If 10 c. c. of sample is used and the nitrate solution has been made up by dissolving 27.09 grams of chemically pure, dry silver nitrate crystals per liter of solution, then the reading of the burette when the color change occurs will be numerically equal to the salinity of the sample.

The assumption is made here that the silver nitrate crystals are 100 per cent silver nitrate and that 55.25 per cent of the total dissolved solids is chlorine. This proportion is in close agreement with Dittmar's figures on the composition of average sea water and with the data in Clarke's The Data of Geochemistry, and in fair agreement with Knudsen's formula:

$$\text{Salinity} = 0.030 + 1.8050 \times \text{chlorine content}$$

where salinity and chlorine content are both expressed in parts per thousand by weight.

Figure 3 shows the outfit needed for the chemical titration method. The locker can be constructed by the ship's carpenter from Figure 3. The dimensions given in the figure correspond to those of the locker made up in the office for tryout on board the *Lydonia;* the height can be reduced by 4 inches, the width by 2 inches, and the depth by 1 inch, if necessary; all measurements are inside measurements. The following chemical apparatus will be needed and can be purchased from any laboratory supply house:

One half-gallon aspirator bottle, plain.
One one-hole rubber stopper for aspirator bottle.
NOTE.—Some aspirator bottles require 2 rubber stoppers, 1 at the mouth and 1 at the outlet.
One rubber bulb, with hard-rubber valves, for pressure.

One length soft glass tubing, about ¼ inch inside diameter.
Two feet rubber tubing, black, pure gum, heavy wall, ¼ inch inside diameter.
One burette, 50 c. c., plain (for use with pinch cock).
One plain rubber stopper to fit top of burette.
One burette attachment, for refilling from reservoir, consisting of glass tip, T-tube, rubber connections, and 2 pinch cocks.
One glass tube, elbow shape, about ¼ inch inside diameter, 1½ inches straight tubing on each leg. This can be made on board by the use of a blow torch, if desired.

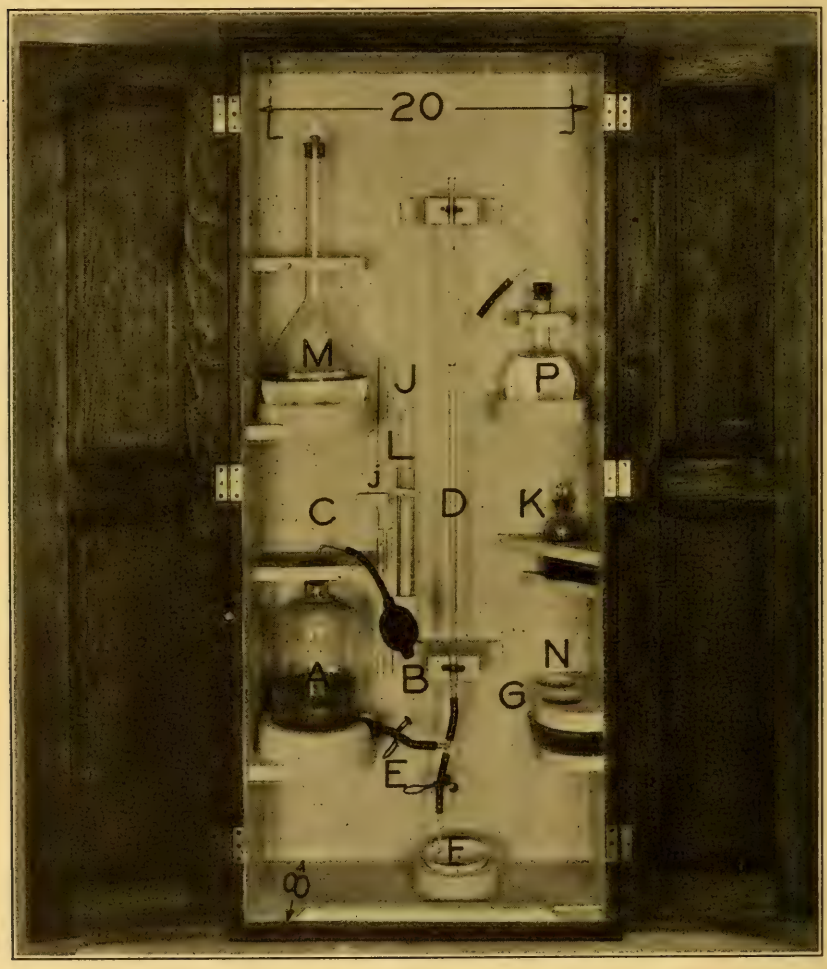


FIG. 3.—Chemical titration outfit

Two beakers, pyrex glass, 150 c. c.
One evaporating dish, 250 c. c.
One washing bottle, pyrex, complete, 500 c. c.
One glass stirring rod.
One transfer pipette, 10 c. c.
One transfer pipette, 1 c. c.
One bottle, tincture, 4 ounce, with glass stopper.
One volumetric flask, 2 liters.

The arrangement of the apparatus should be clear from the figure. Glass tubing is cut by marking it with a three-cornered file, placing the thumb-nails opposite the file mark and pulling the ends apart with a slight inclination away from the scratch. Raw ends of glass tubing should be "fire polished" by heating to redness in a blowtorch flame.

It will be found convenient to set the evaporating dish in a wooden block mounted in a set of boat-compass gimbals. This has not been done in the outfit shown in Figure 3. The parts of the apparatus, all of which appear in the figure, are designated there as follows:

A.—Aspirator bottle (for silver nitrate solution).

B.—Rubber pressure bulb (for developing a slight air pressure in the aspirator bottle).

C.—Glass elbow tube.

D.—Burette (should be fitted with plain rubber stopper at top).

E.—Parts of burette attachment.

F.—Evaporating dish (the wooden block shown may be mounted in boat-compass gimbals; if the locker is made of the height shown in the figure, there will be plenty of room for this change).

G.—Beaker (for supply of sea-water sample).

H.—Stirring rod (not shown in the figure; should be where *J* is).

J.—Transfer pipette, 10 c. c., for measuring out sample of sea water (out of place in the figure; should be in position *j*).

K.—Tincture bottle (for supply of potassium chromate indicator).

L.—Transfer pipette, 1 c. c. (for adding potassium chromate, indicator to measured portion of sea-water sample in the evaporating dish).

M.—Volumetric flask, holding exactly 2 liters of solution to etched mark in neck (for use in preparing silver nitrate solution).

N.—Extra beaker (for use in preparing silver nitrate solution).

P.—Wash bottle (to be kept filled with distilled water).

Before the apparatus is assembled all tubing, stoppers, and containers should be carefully washed and then well rinsed with distilled water.

The silver nitrate solution must be precisely of the strength already mentioned, 27.09 grams of silver nitrate per liter of solution—54.18 grams for one filling of the volumetric flask. Enough silver nitrate solution for 50 to 60 titrations can be prepared quite easily as follows:

Making sure that the wash bottle and volumetric flask are clean, fill the wash bottle and partly fill the volumetric flask with distilled water so that the volumetric flask can still receive at least a beakerful of solution below the mark in the neck. See that the beaker reserved for silver nitrate is clean, rinse it with distilled water, and carefully empty the weighed portion of silver-nitrate crystals into the bottom of it. Using the wash bottle, carefully rinse the inside of the bottle that held the crystals and pour all the rinse water into the beaker.

Carefully wash down the inside of the sides of the beaker by means of the wash bottle and get the crystals into solution with as little agitation and as little water as possible. Pour the solution carefully

into the volumetric flask, rinse out the beaker carefully with the wash bottle, and pour the rinsing water into the volumetric flask. Rinse down the inside of the neck of the flask with the wash bottle. Carefully fill the flask with distilled water up to the mark in the neck so that the mark is just tangent to the bottom of the meniscus.

If these instructions have been carried out with reasonable care, the solution will be quite accurately of the required strength. The rubber stopper and bulb may now be removed from the top of the aspirator bottle and the silver-nitrate solution poured in, making sure beforehand that both burette pinch cocks are closed. Replace the rubber stopper and bulb into the aspirator bottle, pump up a little air pressure, loosen the rubber stopper in the top of the burette, and by means of the upper pinch cock fill the burette partly full of solution. Place the beaker that is reserved for silver-nitrate solution under the burette and allow solution to run into it until all parts of the burette attachment, especially the glass tip, are full of solution, with no air bubbles.

Again remove the rubber stopper and bulb from the top of the aspirator bottle, pour into the bottle the solution that has run down into the beaker, and replace securely the rubber stopper and bulb in the top of the bottle and the rubber stopper in the top of the burette.

The purpose of the rubber stopper in the top of the burette is to prevent evaporation. It must be loosened when the apparatus is in use, but must be kept securely in place when the apparatus is not in use.

Silver-nitrate crystals undergo chemical change when exposed to unfiltered sunlight, and it is for this reason that they are usually stored in amber-colored glass bottles. This colored glass seems to protect them quite effectively from the short, chemically active light waves. Care should be taken that the crystals are not exposed to the light unnecessarily.

Silver-nitrate solution apparently does not deteriorate seriously under the action of light. J. W. Sale, of the Food, Drugs, and Insecticides Administration, says that they keep their solution in a clear-glass bottle exposed to light and that the solution appears to keep its strength indefinitely. He calls attention, however, to the recommendation in the United States Pharmacopœia that silver nitrate volumetric solution be kept in an amber-colored, glass-stoppered bottle. An article by A. H. Clark, in the Journal of the American Pharmaceutical Association, volume 1, 1912, page 228, states that a tenth-normal solution of silver nitrate was standardized in December, 1909, and when restandardized two years and eight months later was found to have the same concentration to the fifth significant figure. The solution apparently had been kept in an amber-colored, glass-stoppered bottle during the interval. It is considered quite safe, however, to keep the solution in a clear-glass aspirator bottle, especially since it will be exposed to light only when the apparatus is in use and the locker is open.

It must be admitted that the use of rubber connections in the apparatus is not desirable. Several chemists have stated, however, that trouble from this source is not likely if the glass tubes are placed close together at the rubber

connections, because the solution need not be kept for long periods. It might be well to keep a large portion of a given sample of sea water and determine its salinity at intervals with the apparatus. If the nitrate solution deteriorates, there will be an apparent increase in the salinity of the sample. The chemical titration outfit here proposed may undergo many improvements. For example, it may be found advantageous to use a Squibbs's automatic burette, which could be connected to the aspirator bottle in such a way that the solution would not come into contact with anything except glass. In the meantime, while rubber connections are used, they should be renewed whenever the rubber ceases to be pliable.

The potassium chromate solution must be made up with chemically pure chromate and good distilled water. Its concentration need not be precise, however, and it may be made up by a pharmacist or other competent person, as follows: Dissolve 5 grams of chemically pure potassium chromate crystals in less than 100 c. c. of distilled water. Add silver nitrate solution slowly until a blood-red precipitate is formed that does not disappear upon stirring. Filter and add enough distilled water to the filtrate to make 100 c. c. of solution. This solution should be kept in tincture bottle *K*.

The outfit should now be ready for use. The procedure for determining the salinity of a given sample of sea water is as follows:

1. Place some of the sample in the beaker that is toward the front of the case. Rinse the evaporating dish, 10 c. c. pipette, and stirring rod with some of the sample and then shake them clear of rinsing water.

2. Pump up a little pressure in the aspirator bottle and loosen the rubber stopper at the top of the burette. Fill the burette with silver nitrate solution, controlling the flow by means of the left-hand pinchcock until the zero mark on the burette is precisely tangent to the bottom of the meniscus of the nitrate solution.

3. Using the 10 c. c. pipette, measure out 10 c. c. of sea-water sample into the evaporating dish. Using the 1 c. c. pipette, add about ½ c. c. of potassium chromate solution.

4. Allow silver nitrate solution to run down into the evaporating dish from the burette, stirring constantly, until a red tint appears that does not disappear upon stirring. The reading of the burette at the bottom of the meniscus will then be the salinity of the sample in parts per thousand (by weight) of total dissolved solids.

The solution should be stirred vigorously near the "end point" to coagulate the white precipitate of silver chloride and soak out the sodium chloride.

The observer can usually estimate a minimum value for the salinity and let the nitrate solution run out of the burette rapidly down to the mark on the burette corresponding to the estimated minimum salinity. After that he should let the nitrate drip down drop by drop. Possibly one or more drops will come down after the color

change occurs. The observer should subtract 0.05 c. c. from the burette reading for each of these drops (including the one left hanging from the tip of the burette).

5. Replace the rubber stopper snugly in the top of the burette. Rinse the beaker, evaporating dish, stirring rod, and 10-c. c. pipette with fresh water or distilled water (from the wash bottle), and the 1-c. c. pipette with *distilled water.*

The apparatus will then be ready for the titration of the next sample.

Experiments were conducted on board the *Lydonia* to determine how consistent would be the values obtained for the salinity of a given sample by the above method by several officers that were wholly inexperienced in titrations. Each one made his determination independently, without knowing the results obtained by the others. The ship was rolling 10° to 15°. The results are shown in Table 3. It is reasonable to expect that the results would be more concordant after each of the officers had made a few titrations.

TABLE 3.—*Independent observations of the salinity of a given sample of sea water by the chemical titration method*

Observer No.	Burette reading at end point, c. c.	Salinity of sample
1	34. 4	34. 4
2	34. 3	34. 3
3	34. 65	34. 65
4	34. 4	34. 4
5	34. 5	34. 5

NOTE.—The first three observers had had no previous experience with this method.

Professor Giral[1] states that variation in the proportion of chlorine in the total dissolved solids in different regions is such that no more than three significant figures are justified in salinity values computed from the results of chlorine titrations. From data obtained from Clarke's The Data of Geochemistry it has been estimated that the variation from 55.25 per cent chlorine in total dissolved solids may cause an extreme error of three or four units in the third significant figure but not more than one unit in the third significant figure in the waters along the Atlantic and Pacific coasts of the United States.

While the method described above will doubtless meet all the needs of the echo-sounding work of the United States Coast and Geodetic Survey, attention is called to the more precise, although somewhat more difficult, technique involving the use of the salinity outfit supplied by the Copenhagen Laboratory of the Conseil permanent inter-

[1] Conseil permanent International pour l'Exploration de la Mer. Publication de Circonstance No. 90.

national de la Mer. This apparatus is used by the United States Geological Survey, the Bureau of Fisheries, and other organizations. The outfit is described briefly by Dole and Chambers in Carnegie Institution Publication No. 213, 1918, page 309, as follows:

> An essential part of the apparatus is a calibrated burette so graduated that its reading is approximately grams per kilogram of chloride if 15 c. c. of sea water is titrated with a solution containing about 37 grams per liter of silver nitrate. A float in the burette assists in estimating tenths of the smallest divisions. The strength of the standard solution of silver nitrate is determined by carefully analyzed sealed tubes of standard sea water supplied by the Copenhagen Laboratory as a necessary part of the outfit. The apparatus is designed and constructed with the object of attaining maximum accuracy in titration. Special precautions observed in titration are precise measurement of the sample in an automatic pipette, vigorous stirring of the liquid by means of a glass rod flattened at the end, and observation of exactly similar tints as end points.

DIPPING REFRACTOMETER METHOD

Figure 4 shows the Bausch & Lomb dipping refractometer, together with the heating trough and some of the glass cups (test tubes) into which the samples of liquid to be tested are placed. The dipping refractometer affords a convenient means of determining the salinity of sea water with fair precision, and it can be used satisfactorily on board ship in very rough weather. The instrument is designed to measure the refractive indices of liquids at known temperatures but must be used in connection with calibration charts, since it gives indications directly only in terms of an arbitrary scale.

Looking into the telescope of the instrument the observer sees part of the field illuminated and part dark, with the dark and illuminated parts quite sharply separated along a chord in the focal plane of the objective. In the focal plane of the objective is mounted also a scale graduated from 0 to 100. By means of a micrometer screw the observer can measure to four significant figures the position on the scale of the chord of separation.

The Coast and Geodetic Survey has purchased one of these instruments, and a careful preliminary calibration has been made, both for sea water and for boiler water. This preliminary calibration was carried out in July, 1927, as follows:

A quantity of sea water of average composition was taken from the Atlantic Ocean off Beaufort, N. C., and divided into four portions; the first portion was left as it came and was of salinity 33.90; the second was partially evaporated to salinity 40.22; the third was diluted to salinity 31.25; the fourth was diluted to salinity 5.34. These four samples were standardized by the Food, Drugs, and Insecticides Administration, both by chemical titration for chlorine content and by pycnometer for density.

Each of the four samples and a sample of distilled water was run several times with the refractometer from 3° to 26° C. The results

with the 31.25, the 33.90, and the 40.22 samples were plotted on one sheet, with scale readings as abscissas and temperatures as ordinates;

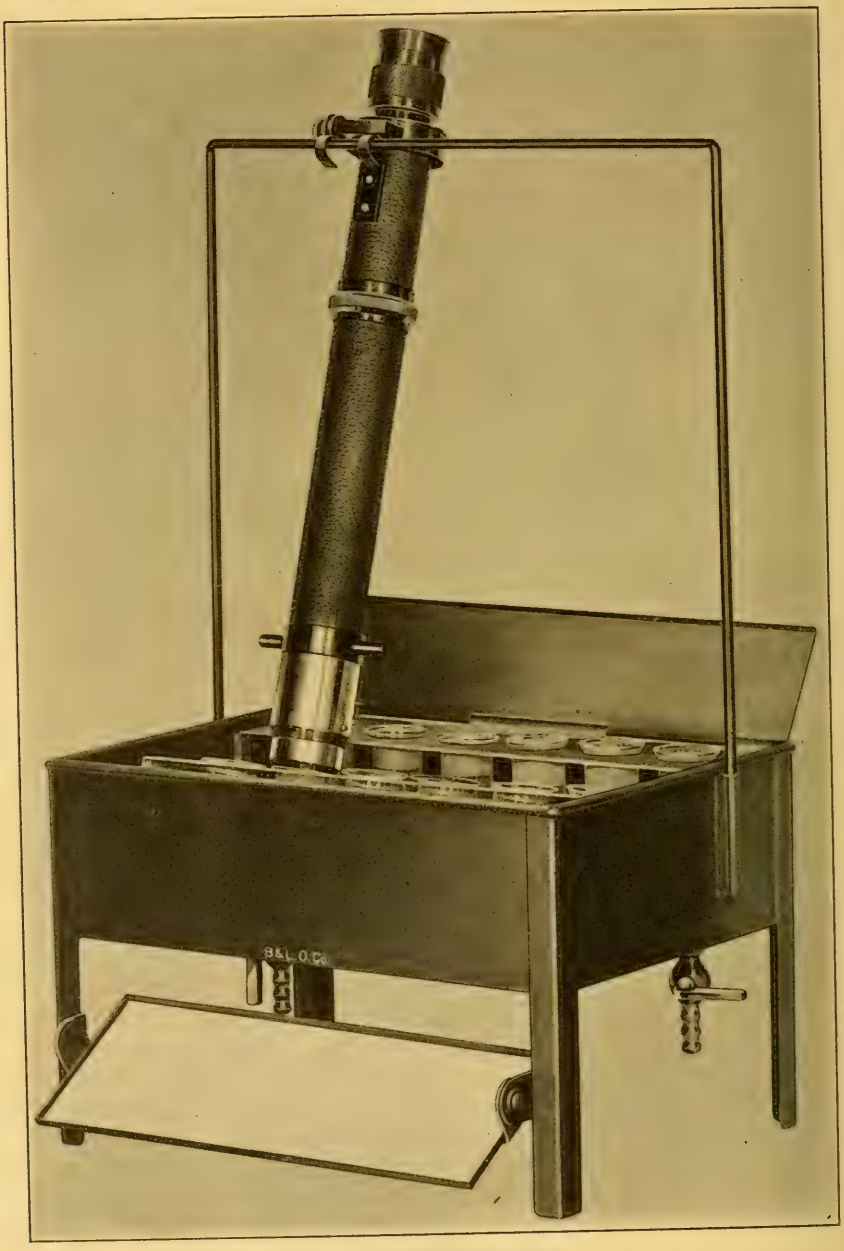
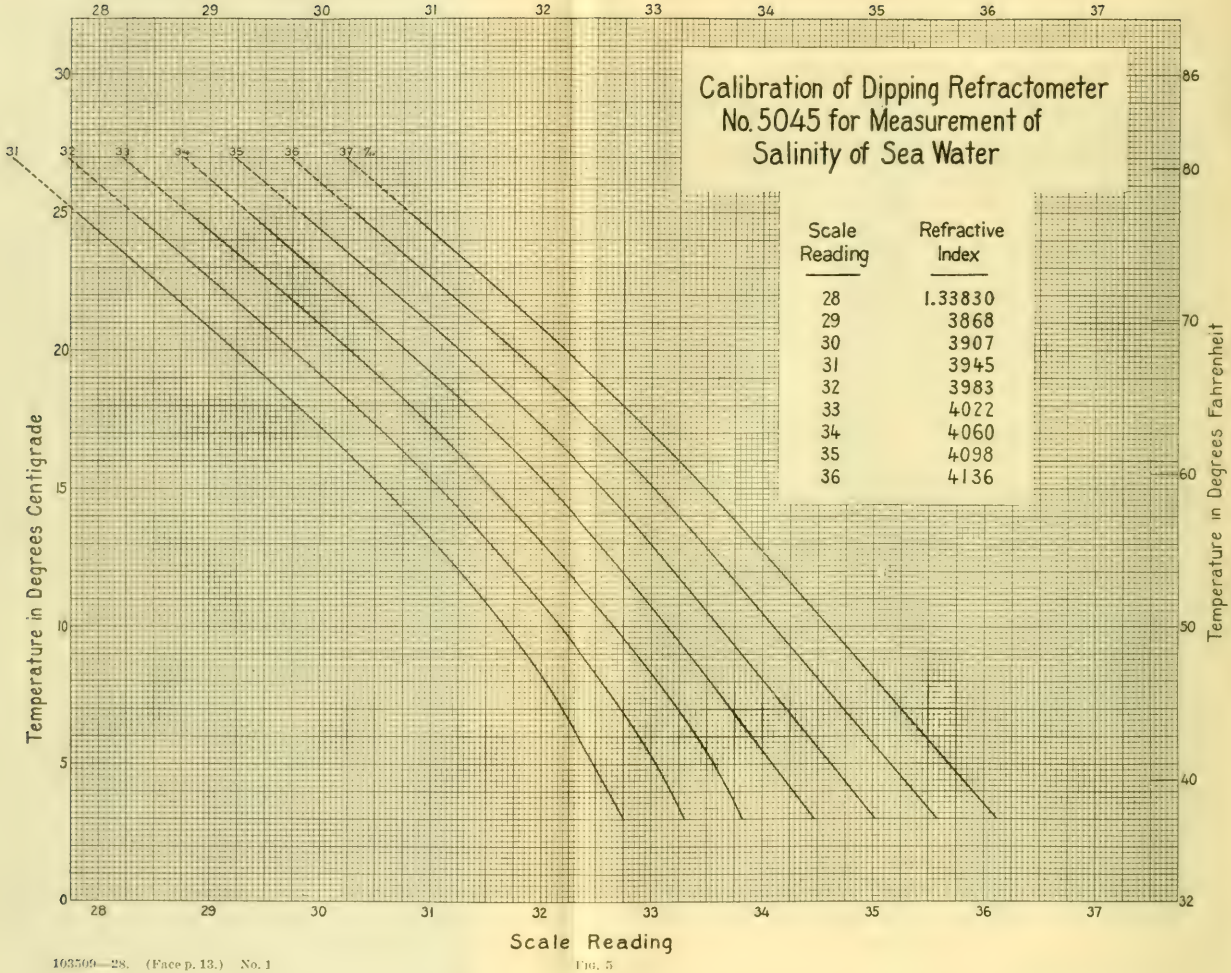


FIG. 4.—Dipping refractometer

the results with distilled water and the 5.34 sample were plotted on another such sheet. By interpolation between the 31.25, 33.90, and



163509—28. (Face p. 13.) No. 1

FIG. 5

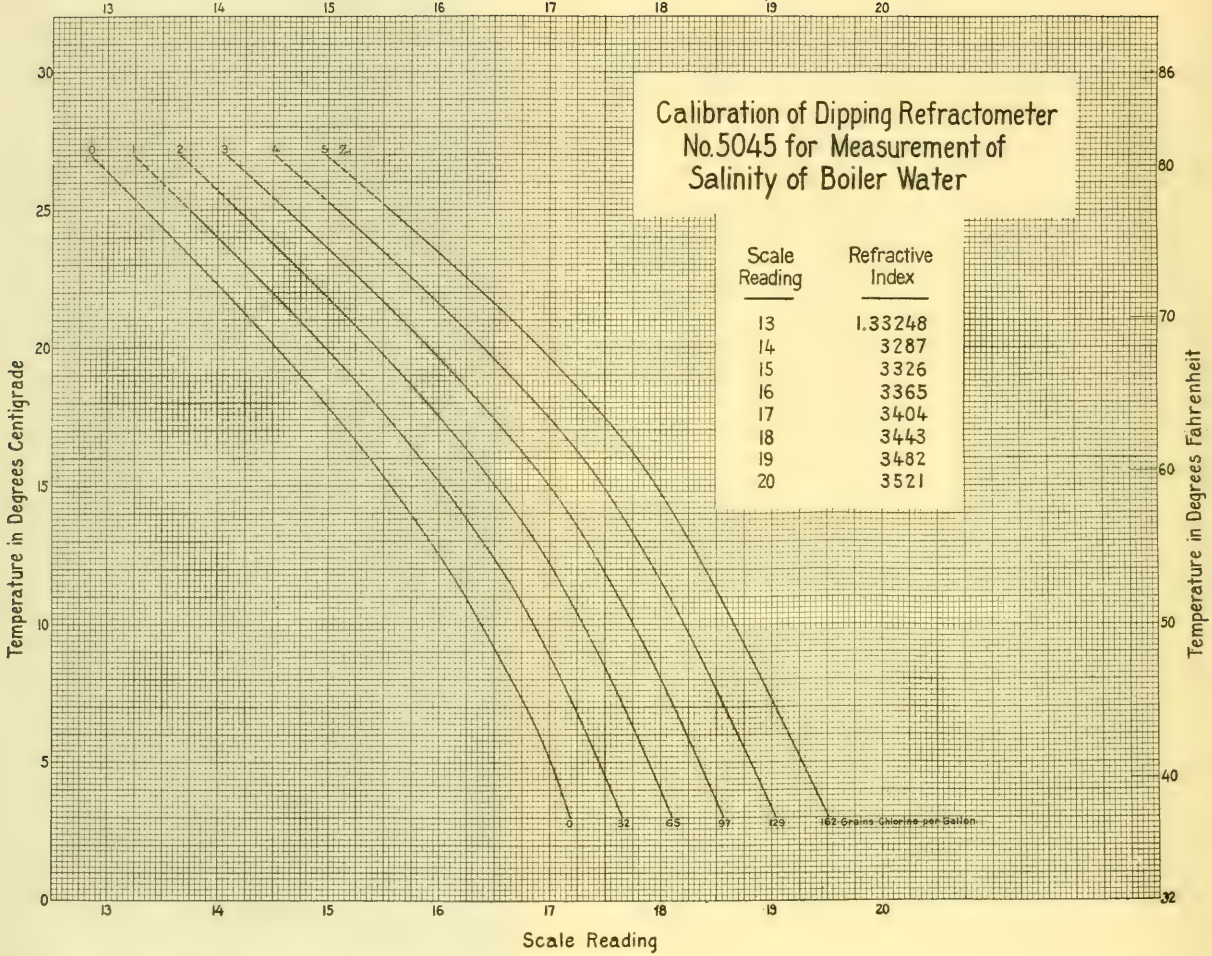


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FIG. 6

40.22 curves, curves for sea water of salinities 31, 32, 33, 34, 35, 36, and 37 parts per thousand were obtained; by interpolation between the distilled water and the 5.34 curves, curves were obtained for boiler water of salinities 0, 1, 2, 3, 4, and 5 parts per thousand, corresponding to 0, 32, 65, 97, 129, and 162 grains chlorine per gallon.

These sea-water and boiler-water curves are given in Figures 5 and 6, respectively. Correspondence with the manufacturers indicates that calibration charts applying to one dipping refractometer will apply to any refractometer of the same type within about two units in the third figure of salinity, provided the instruments are adjusted to agree on some one sample at a given temperature.

So far as it has been possible to test the curves before this publication was prepared, they have given salinities in fair agreement with results obtained by chemical titration. The curves should be regarded as preliminary, however, because they are not based upon a large variety of samples. Extended experiments with the refractometer to a large number of samples, which will be standardized by the pycnometer method, will doubtless give more precise curves.

The following procedure is recommended for the use of the dipping refractometer. In fairly smooth weather so that it is feasible, the instrument should be used in connection with the heating trough and small glass cups supplied with the instrument, because such procedure insures more accurate temperature determination. The trough should be filled with fresh water, at about room temperature, nearly to the top of the overflow pipe. Two of the cups should be filled about half full of the sample, after being well rinsed with sample, and placed side by side in the center rack. The prism of the refractometer should be dipped into one cup and then placed in position in the other cup ready for observing. The thermometer should be suspended in the cup not occupied by the prism.

After allowing the instrument to stand for two or three minutes, for the temperature of the two portions of sample to come to that of the water bath, a series of 10 observations should be taken of the position on the scale of the chord separating the dark and illuminated portions of the field, the thermometer being read on the first, fifth, and tenth scale readings. The proper graduation on the scale should be brought into coincidence with the chord of separation alternately from above and from below.

From the mean of the 10 scale readings and the mean of the three temperature readings the salinity of the given sample can be read off the calibration chart. The observer looks out the point on the chart corresponding to the mean scale reading and the mean temperature. If, for example, this point falls seven-tenths of the distance, measured parallel to the axis of scale readings, from the

35 curve to the 36 curve, the salinity of the sample is 35.7. When the test has been completed, the prism should be dipped into fresh water and brushed dry with a clean, soft cloth. The glass cups and the thermometer should also be rinsed with fresh water.

If the weather is such that the water tends to slop out of the heating trough, so that the latter can not be used conveniently, the cup designed for use with volatile liquids, which is supplied with the instrument, can be used. The test should be performed in a closed room in order that it may be possible to determine the temperature of the sample with some degree of certainty. The cup should be filled about half full of sample and then allowed to stand for two or three minutes, after which the temperature of the sample in the cup should be taken.

The cup is then fitted to the end of the refractometer, the latter pointed toward the light, and five scale readings taken. The cup is then removed from the refractometer and the temperature of the sample in the cup again observed. From the mean of the five scale readings and the mean of the two temperature readings the salinity of the sample can be obtained from the chart. The cup should be rinsed out with fresh water after the test and the prism and thermometer also cleaned as already explained.

Experiments were conducted recently on board the *Lydonia* to determine the consistency of values of the salinity of a given sample obtained by means of the refractometer by several inexperienced observers working independently of one another. The results are given in Table 4. After the observers had a little practice with the instrument their individual results would be, no doubt, in better accord with one another.

TABLE 4.—*Independent determinations of the salinity of a given sample of sea water by the dipping refractometer method*

Observer No.	Scale reading	Temperature °C.	Salinity
1	30. 53	22. 6	35. 0
2	30. 53	22. 6	35. 0
3	30. 75	22. 2	35. 2
4	30. 86	21. 95	35. 3
5	30. 39	22. 95	35. 0
6	30. 84	22. 0	35. 3
7	30. 80	22. 0	35. 2
8	30. 75	22. 6	35. 5
9	30. 64	22. 6	35. 3
10	30. 68	22. 4	35. 2

NOTE.—With the exception of the last observer, none of the observers had had any previous experience with the method. The observations were made on board the Lydonia while she was under way and rolling 10° to 15°.

OTHER METHODS FOR USE ON BOARD SHIP

ELECTRICAL CONDUCTIVITY METHOD

Probably the most precise method for measuring the salinity of sea water, either on board ship or in the laboratory ashore, is by the electrical conductivity apparatus developed by Dr. Frank Wenner, of the United States Bureau of Standards. This apparatus has been used principally by Commander Edward H. Smith, United States Coast Guard, and is described in Bulletin No. 12 of the International Ice Observation and Ice Patrol Service in the North Atlantic Ocean, Season of 1924. Although the apparatus is rather expensive and more precise than the needs of the Coast and Geodetic Survey require, so that it will probably not come into use in this bureau, it gives salinity to five significant figures and is fairly convenient to use. For the details of this apparatus and the procedure involved in its use, the reader is referred to the above-mentioned publication of the Coast Guard.

One of the early steps in the development of the Wenner apparatus was the work of Weibel and Thuras, described in the Journal of the Washington Academy of Sciences, Volume VIII, page 145, 1918. They describe, in this article, an electrical conductivity apparatus, which when installed on board a ship will make a continuous record of the salinity of the surface water passed through by the ship.

Dr. G. Guében, of the University of Liege, Belgium, is doing some interesting work in the measurement of the salinity of sea water by electrical methods. It involves the measurement of the specific conductivity of sea water in place; that is, by lowering a pair of electrodes to the desired depth, and not by bringing up a sample and measuring its conductivity on board. The work of Monsieur and Madame Chauchard, published in the Comptes Rendus de l'Académie des Sciences, tome 185, page 1503 (December 19, 1927), is also of interest.

Monsieur and Madame Chauchard also proceed by measuring the specific conductivity of the water in place by lowering a conductivity cell inclosed in a glass cylinder to the desired depth. The glass cylinder has clack valves at its upper and lower ends and contains a thermometer alongside the conductivity cell. When the apparatus is hauled up after the measurement of conductivity, the clack valves close, and thus the thermometer is brought up immersed in a sample of water from the depth in question and the temperature at that depth can be read off.

Sir John Murray and Dr. Johan Hjort, in The Depths of the Ocean (Macmillan, London, 1912), make mention of salinity meas-

urements by Knudsen by a conductivity method similar to that of Monsieur and Madame Chauchard. They state that Knudsen obtained good results in shallow water.

A device patented by Alexander McNab is described in Marine Engineering and Shipping Age, for May, 1927, which operates on the electrical conductivity principle and gives a continuous indication of the salinity of the boiler feed water on board ship.

Regarding the relative conductivities of water samples of various salinities, Monsieur and Madame Chauchard state that they found a change of resistance from 6.3 ohms for sea water to 450 ohms for fresh water from the laboratory tap. In the summer of 1927 the writer measured the resistance at 24.°6 C. of the four samples of sea water used in the refractometer calibration described earlier in this publication. Measurements were made on a Leeds-Northrup portable test set with an alternating-current source and with phones as balance indicator. As electrolytic cell, the tube shown in Figure 7 was used. The results of the measurements are shown in Table 5.

TABLE 5.—*Variation with salinity at 24.°6 C. of electrical resistance of column of sea water contained in the apparatus shown in Figure 7*

Salinity in parts per 1,000	Resistance in hundreds of ohms
5. 34	365±5
31. 25	71±0. 5
33. 90	66±0. 5
40. 22	56. 5±0. 5

These measurements are described merely to indicate roughly how the conductivity varies with the salinity. However, the indications were that even with this crude arrangement salinity could be measured with an uncertainty not greater than 3 in the third significant figure.

Any conductivity apparatus must be calibrated by means of measurements made with it on samples standardized by other methods.

METHOD OF BALANCING COLUMNS OF LIQUIDS

To test the possibility that the salinity of sea water could be measured on board ship by balancing a column of sea-water sample against a column of some standard liquid, the apparatus shown in Figure 8 was purchased by the Coast and Geodetic Survey and was calibrated at 25° C. in the summer of 1927. Kerosene colored with oil red was used in one arm and the sea-water sample in the other; the two liquids did not come into contact. The method was found to be much more convenient than was expected, a complete set of opera-

tions on a given sample consuming about 10 minutes. The indications were that the method would give results of about the same order of accuracy as a hydrometer and that for use on board ship it would require weather of about the same degree of smoothness as that required for the satisfactory use of a hydrometer.

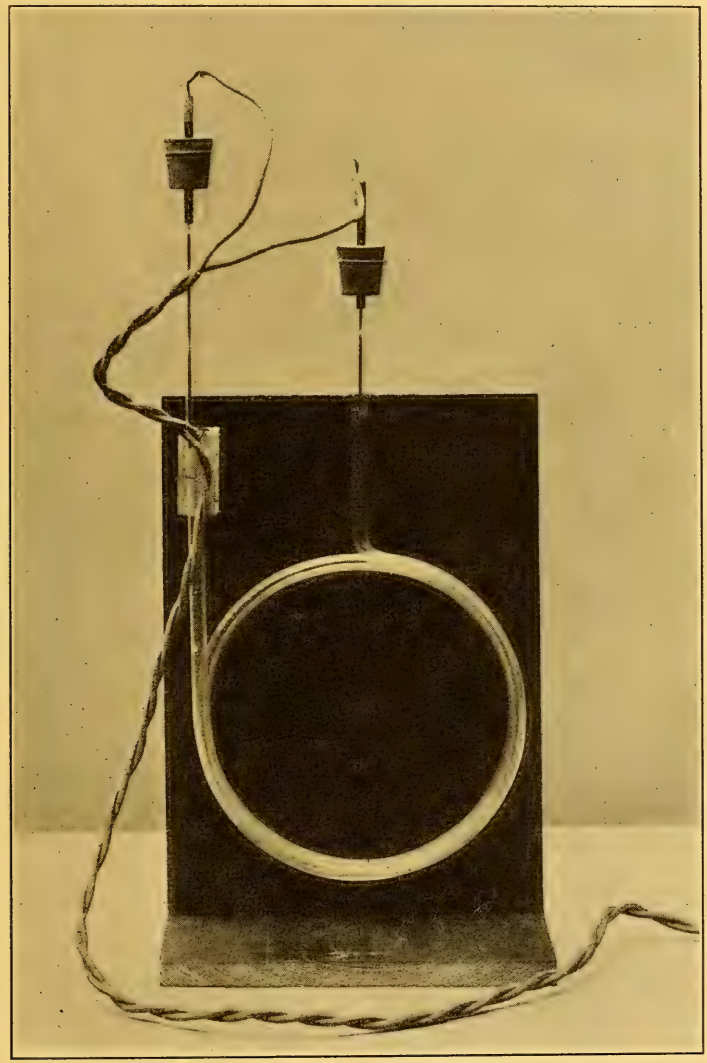

FIG. 7.—Electrolytic cell used for preliminary measurements of resistance of sea-water samples of various salinities

METHODS FOR LABORATORY USE

In addition to the methods described in the preceding, two very precise methods are available. They are not applicable on board ship but can be used in the laboratory. These are the pycnometer

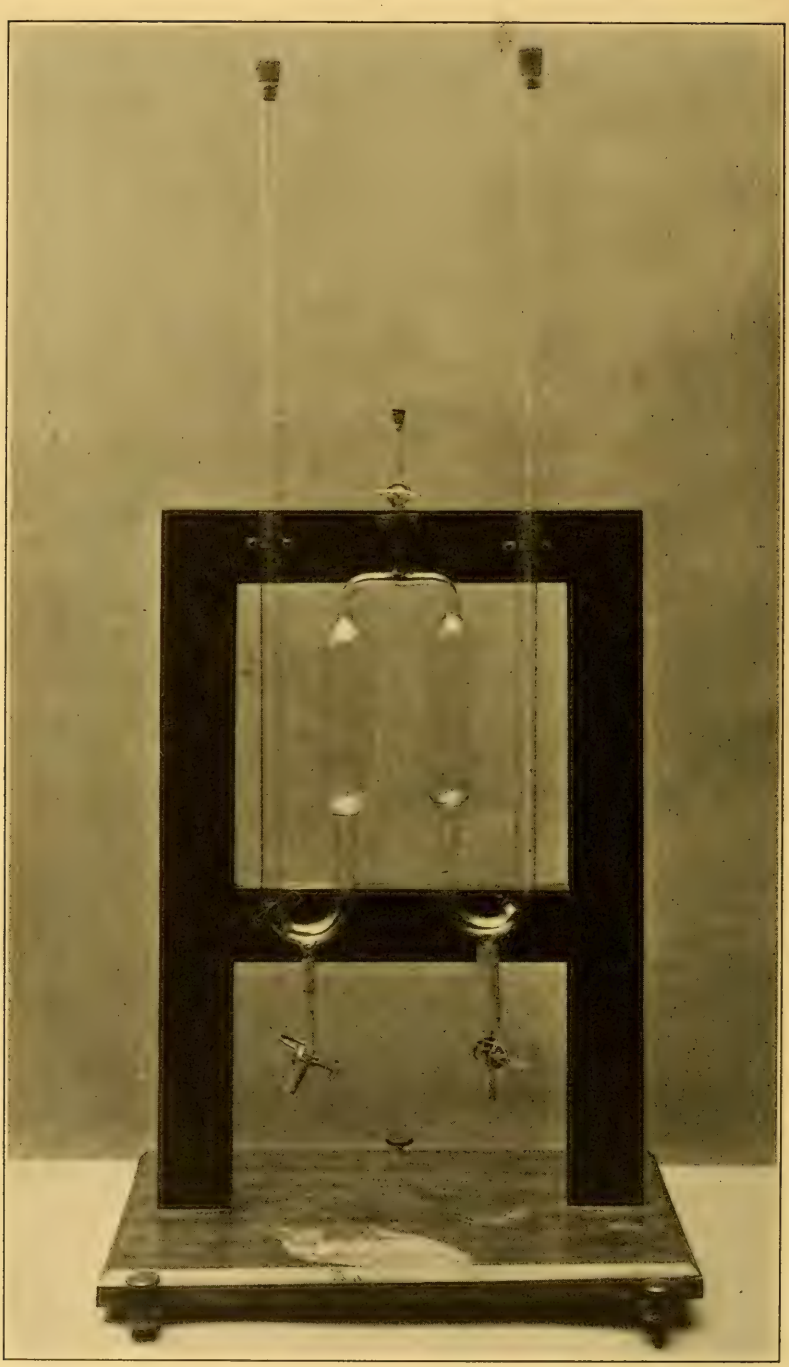

FIG. 8.—Apparatus for measuring salinity by the method of balancing columns of liquids

method and the sinker method, both of which arrive at the salinity of the sample directly through its specific gravity. Either method, when used with reasonably good equipment and with reasonable care, will give salinity with an average error of about 2 in the fourth significant figure.

PYCNOMETER METHOD

In the pycnometer method a small glass bottle with perforated glass stopper is weighed—first, empty and dry; second, full of distilled water at a known temperature; third, full of sea water at a known temperature. From the first two weighings, which can be made once for all, the volume of the sample can be obtained. From the first and third weighings the mass of the sample is determined. From this the specific gravity of the sample can be calculated readily, and its temperature having been measured, its salinity can be obtained.

Table 1 or Figure 2 might be used for this conversion from specific gravity and temperature to salinity, but for precise work, such as is possible with the pycnometer method and with the sinker method, it is better to use Tables 16^{H} to 19^{H}, inclusive, of Dynamic Meteorology and Hydrography, Part I, Statics, by V. Bjerknes and J. W. Sandström, which is Publication No. 88, 1910, of the Carnegie Institution of Washington; or the Hydrographic Tables, by Martin Knudsen, Copenhagen, 1901.

SINKER METHOD

The details of this method, as used by the Scripps Institution of Oceanography, are contained in a paper by N. W. Cummings in the Proceedings of the First Pan-Pacific Science Congress, at Honolulu, 1921. Mr. Cummings also gives several references to papers describing other good available methods for measuring the specific gravity of sea water.

A glass sinker, having a volume of about 25 c. c. and a weight of about 35 g., is suspended by a fine platinum wire, 0.1 mm. in diameter, from the left arm of a chemical balance of sensitivity 0.1 mg. and weighed once for all suspended in distilled water of known temperature. The specific gravity of a given sample of sea water is obtained by weighing the glass sinker in the sample and at the same time determining the temperature of the sample. The portion of the sample in which the sinker is immersed is "held in a specially designed container * * *."

"After the determination is made the sample is withdrawn through a tube leading from the bottom of the containing vessel. It is thus possible to introduce and remove the sample without in any way disturbing the apparatus." The well-systematized procedure, both

of laboratory work and of computation, described by Mr. Cummings in his paper, "makes it possible to run about 30 samples and to correct each specific gravity to the value corresponding to 0° all within one hour."

SALINITY BY EVAPORATION TO DRYNESS

According to Sir John Murray and Dr. Johan Hjort, in The Depths of the Ocean, "the direct determination of salinity by evaporating a known volume of water to dryness does not give accurate results, unless the amount of chlorine is carefully determined before and after the evaporation, because in the last stages of evaporation and in drying the residual salt uncertain amounts of chlorine are disengaged in the form of hydrochloric acid."

Clarke, in The Data of Geochemistry, states that it is principally the magnesium chloride that breaks down during evaporation. In any case this method is not to be recommended, although at first thought it seems to be most straightforward.

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